ACS Sustainable Chemistry & Engineering

Research Article

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Environmental Assessment of Dimethyl Carbonate Production: Comparison of a Novel Electrosynthesis Route Utilizing CO_2 with a Commercial Oxidative Carbonylation Process

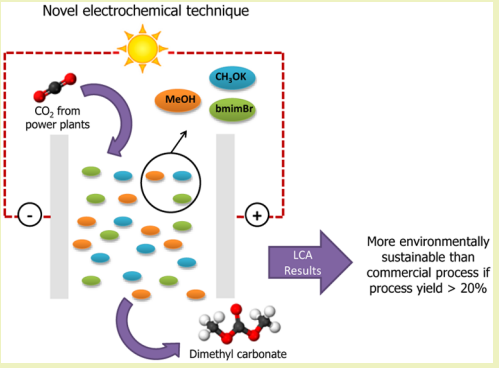
Isabel Garcia-Herrero,*[,†] Rosa Marisa Cuéllar-Franca,[‡] Víctor Manuel Enríquez-Gutiérrez,[‡] Manuel Alvarez-Guerra,[†] Angel Irabien,[†] and Adisa Azapagic[‡]

[†]Universidad de Cantabria, ETSIIT, Department of Chemical and Biomolecular Engineering, Avda. Los Castros s/n, Santander 39005 Spain

[‡]School of Chemical Engineering and Analytical Science, The University of Manchester, The Mill, Sackville Street, Manchester M13 9PL, U.K.

Supporting Information

ABSTRACT: Life cycle assessment (LCA) has been used at an early design stage to evaluate the environmental sustainability of a novel process for synthesizing dimethyl carbonate (DMC) from waste CO_2. The process involves an electrochemical reaction of CO_2 and methanol in the presence of potassium methoxide and the ionic liquid 1-butyl-3-methylimidazolium bromide to produce DMC. Experimental data and process simulation have been combined to estimate the environmental impacts and compare them to the conventional commercial "Eni" process based on oxidative carbonylation of methanol. Eleven environmental impact categories have been assessed from "cradle to gate", including global warming potential (GWP), toxicity potentials, and resource depletion. For example, GWP of DMC produced in the electrochemical process ranges from 63.3 to 94.5 kg CO_2 eq./kg DMC, depending on a process configuration. This is around 25 times higher than GWP of the commercial process estimated in this study at 3.2 kg CO_2 eq./kg DMC. This is because of the low conversion achieved in the current design of the electrochemical process (0.7%), requiring high energy consumption in the separation process. The results suggest that the process yield must be increased to at least 20% to reduce the GWP to a level comparable with the commercial process. At this yield, the electrochemical process also becomes more sustainable than the commercial system for most other impacts considered. The study demonstrates how LCA can play a key role in the development of environmentally more sustainable processes during design by combining experimental data and process simulation at an early stage of technology development.



KEYWORDS: *Dimethyl carbonate, Carbon capture and utilization, Climate change, Life cycle assessment, Oxidative carbonylation*

INTRODUCTION

Dimethyl carbonate (DMC) is an alkyl carbonate [$(CH_3O)_2CO$] which can be used in different applications. More than 90 000 t/y is consumed globally, largely as an intermediate in the production of polycarbonates (~50%) and as a solvent (~25%).[1,2] DMC can also act as a substitute for toxic phosgene and methylating agents (e.g., methyl sulfate and methyl chloride) and as an emission-reducing additive to fuels, substituting methyl *tert*-butyl ether.[3]

DMC can be produced by six different routes, summarized in Table 1. The traditional manufacturing process involves the use of phosgene (route I in Table 1[4]), which has been progressively replaced by less toxic routes based on oxidative carbonylation of methanol (II and III).[5,6] The Eni process (formerly known as Enichem) is currently the most prevalent commercial pathway for the production of DMC (99.8% purity) through oxidative carbonylation of methanol using O_2 (route II) and accounts for nearly 85% of Europe's production.[5,7] The Ube process (route III) is also based on the carbonylation of methanol but uses NO_x instead of O_2;[6] it contributes 11% to the DMC market.[8] In addition, new alternative processes for DMC are being studied, including transesterification of ethylene carbonate (route IV) which was setup at a commercial scale in the early 2000s by Asahi (as described in ref 9) transesterification of urea (route V[10]) and direct synthesis from CO_2 (route VI[11]). The latter is arguably the most attractive option, as it allows the use of waste CO_2 captured from power plants or other industrial sources as a feedstock for the production of chemicals such as DMC. However, one of the main limitations of such carbon capture and utilization (CCU) processes is the large energy requirement for CO_2 conversion because of its high thermodynamic stability.[12] Electrochemical techniques could represent a

Received: November 17, 2015
Revised: February 26, 2016
Published: March 7, 2016

DOI: 10.1021/acssuschemeng.5b01515
ACS Sustainable Chem. Eng. 2016, 4, 2088−2097

Table 1. Routes for DMC Production

route	description	reactions	reaction conditions T, P	source
I	methanol phosgenation	$COCl_2 + 2\ CH_3OH \rightarrow (CH_3O)_2CO^a + 2HCl$	(−5)−(+30) °C, not reported	Buysch et al.[4]
II	oxidative carbonylation of methanol (Eni)	$CO + 2CH_3OH + O_2 \rightarrow (CH_3O)_2CO^a + H_2O$	70−200 °C (typically 120 °C), 5−60 atm (typically 27 atm)	Romano et al.[5]
III	oxidative carbonylation of methanol via methyl nitrite (Ube)	$N_2O_3 + 2CH_3OH \rightarrow 2CH_3ONO + H_2O$ $2CH_3ONO + CO \rightarrow (CH_3O)_2CO^a + NO$	50−150 °C, 1−10 atm	Nishihira et a.[6]
IV	ethylene carbonate transesterification (Asahi)	$(CH_2)_2O + CO_2 \rightarrow C_2H_4O$ $C_2H_4O + 2CH_3OH \rightarrow (CH_3O)_2CO^a + (CH_2OH)_2$	100−180 °C, 40−60 atm	Omae[9]
V	urea transesterification	$2NH_3 + CO_2 \rightarrow (NH_2)_2CO + H_2O$ $(NH_2)_2CO + CH_3OH \rightarrow CH_3OCONH_2 + NH_3$ $CH_3OCONH_2 + CH_3OH \rightarrow (CH_3O)_2CO^a + NH_3$	170−200 °C, 1−30 atm	Huang et al.[10]
VI	direct synthesis from CO_2	$CO_2 + 2CH_3OH \rightarrow (CH_3O)_2CO^a + H_2O$	160−180 °C, 90−300 atm	Leino et al.[11]

[a]DMC.

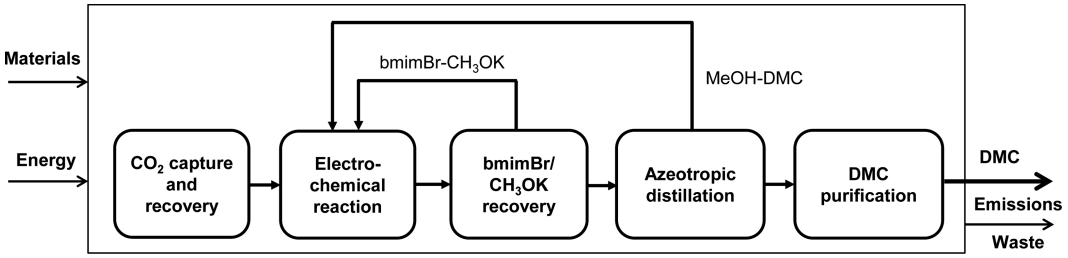


Figure 1. System boundaries for the electrochemical process.

potential solution as they have the ability to supply the necessary energy to activate CO_2 at the ambient temperature and pressure conditions.[13] Several studies are available in the literature on the electrosynthesis of DMC from CO_2 and methanol, especially in the presence of ionic liquids.[14−19]

However, using waste CO_2 as a raw material to produce DMC does not necessarily mean that, on a life cycle basis, the total CO_2 equivalent emissions are lower than those emitted by a conventional process using fossil resources as a carbon carrier. Furthermore, it is not clear how different routes compare for the other environmental impacts, in addition to CO_2 emissions and the related contribution to climate change. Hence, there is a need to evaluate the environmental sustainability of alternative DMC process routes across the whole life cycle and compare them to fossil-based routes. Life cycle assessment (LCA) can be used for these purposes, and several such studies are available in the literature.[20−23] They provide either preliminary screenings of routes I−VI[21,22] or focus on the transesterification of cyclic carbonates[20,22] and urea.[20,22,23] They also usually take phosgenation as a reference process for comparison with the alternative routes, although phosgenation has been progressively substituted by less toxic routes, as mentioned above. As far as the authors are aware, there are no studies that consider life cycle environmental impacts of the currently most widely used commercial carbonylation route (the Eni process). Furthermore, only one LCA study has considered utilization of waste CO_2 to produce DMC, involving a urea-based synthesis, but again in comparison to the conventional phosgene route.[23] In this paper, we focus on an electrochemical route developed recently,[18,19] using electrosynthesis of DMC from waste CO_2 and methanol in the presence of potassium methoxide (CH_3OK) and the ionic liquid 1-butyl-3-methylimidazolium bromide (bmimBr). The aim is to evaluate its environmental sustainability in comparison to the carbonylation route using O_2 and identify improvement opportunities for further process development. The study also shows how LCA can be combined with experimental and process simulation data at an early design stage to facilitate development of processes that are environmentally more sustainable by design.

METHODOLOGY

The LCA study has been carried in accordance with the ISO 14040/44 methodology[24,25] and follows some of the recommendations made in previous LCA studies.[26−29] GaBi V4.4[30] has been used for the LCA modeling and the CML 2001 impact assessment method[31] to estimate the following 11 environmental impacts: global warming potential (GWP), abiotic depletion potential of elements ($ADP_{elements}$), abiotic depletion potential of fossil resources (ADP_{fossil}), acidification potential (AP), eutrophication potential (EP), human toxicity potential (HTP), terrestrial ecotoxicity potential (TETP), freshwater aquatic ecotoxicity potential (FAETP), marine aquatic ecotoxicity potential (MAETP), ozone layer depletion potential (ODP), and photochemical oxidants creation potential (POCP).

Goal and Scope of the Study. The main goal of the study is to quantify the life cycle environmental impacts of the electrochemical process for the synthesis of DMC from waste CO_2 and methanol in the presence of CH_3OK and the task-specific ionic liquid bmimBr[18,19] and to compare it to the commercial oxidative carbonylation of methanol to produce DMC.[5] As mentioned earlier, the latter is known as the Eni process (see the Introduction). A further goal is to identify "hot spots" and opportunities for improvements for the new process route at the design stage. Given that the electrochemical route utilizes waste CO_2 as a raw material, the emphasis is on GWP to ensure the overall positive carbon balance, i.e. that the overall CO_2 eq emissions are not higher than the amount of CO_2 saved by its utilization in the process. However, the above-

DOI: 10.1021/acssuschemeng.5b01515
ACS Sustainable Chem. Eng. 2016, 4, 2088−2097

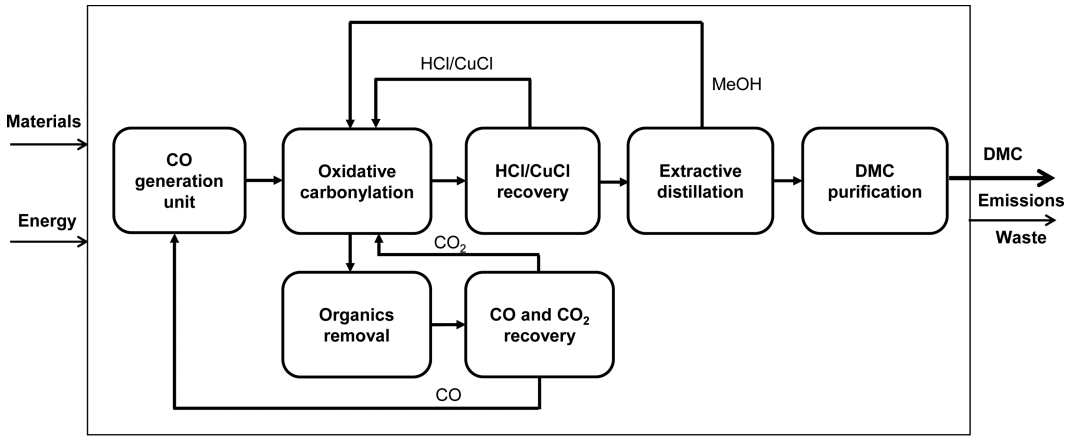


Figure 2. System boundaries for the oxidative carbonylation (Eni) process (based on information from ref 36).

mentioned impacts are also estimated to gauge the additional "penalty" to the environment while trying to reduce the impact on climate change.

As the focus of the study is on the production process, the scope of the study is from "cradle to gate". The system boundaries for the electrochemical process are outlined in Figure 1 and for the conventional process in Figure 2; each route is described in turn in the following sections.

The functional unit is defined as the "production of 1 kg of pure DMC", to match the DMC purity of 99.8% w/w in the commercial processes.

System Description. *Electrochemical Process.* As indicated in Figure 1, the electrochemical route involves the following five steps: CO_2 capture and recovery, electrochemical reaction, recovery of CH_3OK and bmimBr, extractive distillation, and DMC purification. It is assumed that CO_2 is sourced from a coal-fired power plant equipped with a postcombustion CO_2 capture unit using monoethanolamine (MEA). The captured CO_2 is stripped from MEA at high temperature and passed through a filter-press electrochemical cell with platinum/niobium electrodes to react with methanol in the presence of CH_3OK and bmimBr and form DMC.[19] The MEA is recycled back to the CO_2 capture unit.[32] CH_3OK and bmimBr are recovered in a flash unit and reused in the electrochemical cell. The methanol/DMC mixture creates an azeotrope which is broken by extractive distillation using an entrainer which enhances the relative volatility of the components so that DMC can be separated. Methanol and the entrainer are also recovered by distillation, both of which are recycled in the process. Finally, DMC is distilled to achieve the desired purity (99.8%).

Two alternative entrainers are considered for the separation of the azeotrope: water[33] and aniline.[34] Although the latter is toxic (category 2 carcinogen, category 2 mutagenic, category 1 acute aquatic toxicity[35]), it is the most effective entrainer for the methanol–DMC azeotrope[34] and is therefore considered here as a potentially viable alternative to water.

Oxidative Carbonylation (Eni) Process. The life cycle of the oxidative carbonylation route[36] is illustrated in Figure 2. CO, produced by coal gasification, and methanol react with O_2 in the presence of CuCl as a catalyst to produce DMC. HCl is also introduced in the reactor to compensate chlorine losses. The reaction mixture is then sent to the HCl/CuCl recovery section to separate and recycle them back in the reactor. The rest of the process is the same as in the electrochemical route, with the DMC–methanol azeotrope separated in the extractive distillation and DMC sent to purification; methanol is recycled back to the reactor.

A gas stream is also generated in the reactor, containing the unreacted CO and CO_2 as well as organic compounds such as dimethyl ether, dimethoxymethane, and methyl chloride. The stream is sent to an organics removal section to recover CO and CO_2. The former is recycled back to the reactor and the latter to the coal gasification where CO is produced[36] (see "Waste streams" in Table 3). The remaining stream is incinerated and discharged into the atmosphere.

Life Cycle Inventory. *Electrochemical Process.* The inventory data, provided in Tables 2 and 3, have been obtained from different sources, including experiments and process simulation, our own estimations, literature, and LCA databases.[19,32,37−39] An overview of the experiments and process simulation is given below, followed by a summary of the inventory data.

Table 2. Inventory Data for the Postcombustion Capture of CO_2

flows	amount per kg of CO_2 captured
Materials	
activated carbon (kg)	6×10^{-5}
decarbonized water (kg)	0.8
monoethanolamine (kg)	1.6×10^{-3}
sodium hydroxide (kg)	1.3×10^{-4}
Energy	
electricity (kWh)	0.34
Solid Waste	
capture-related solid waste (kg)	3.2×10^{-3}
spent activated carbon (kg)	6×10^{-5}
Emissions to Air	
ammonia (kg)	3.49×10^{-5}
acetaldehyde (kg)	1.67×10^{-10}
carbon dioxide (kg)	−1
formaldehyde (kg)	2.62×10^{-10}
monoethanolamine (kg)	6.27×10^{-8}
nitrogen oxides (kg)	-3.66×10^{-5}
particulates <2.5 m (kg)	-2.85×10^{-5}
particulates >10 m (kg)	-3.18×10^{-5}
particulates >2.5 m and <10 m (kg)	-3.35×10^{-5}
sulfur dioxide (kg)	-7.71×10^{-4}

DOI: 10.1021/acssuschemeng.5b01515
ACS Sustainable Chem. Eng. 2016, 4, 2088−2097

Table 3. Life Cycle Inventory Data for the Electrochemical and Oxidative Carbonylation Processes

	electrochemical process El-chem. (1)	electrochemical process El-chem. (2)	oxidative carbonylation (Eni) process
Materials (kg/kg DMC)	1.40	1.40	1.61
methanol	0.71	0.71	0.77
carbon dioxide	0.49	0.49	
carbon monoxide			0.52
oxygen			0.30
hydrochloric acid			0.02
aniline		3×10^{-4}	
CH_3OK	0.04	0.04	
BmimBr	0.15	0.15	
platinum	3.1×10^{-8}	3.1×10^{-8}	
niobium	4.8×10^{-7}	4.8×10^{-7}	
Energy (MJ/kg DMC)	1324	968	22.7
electricity	497	497	1.16
electrochemical cell	477	477	
pumping	19.6	19.6	
steam from natural gas	827	471	21.5
Water (m^3/kg DMC)	9	5	0.54
Waste streams (kg/kg DMC)	0.40	0.40	0.31
methanol	0.0014	0.0055	
water	0.201	0.200	0.249
aniline		3×10^{-4}	
organics purge			0.056
carbon dioxide (recovered)			0.301

Electrochemical Synthesis Experiments. The electrochemical process has been developed by Garcia-Herrero et al.[18,19] at a laboratory scale. As mentioned earlier, it consists of a filter-press electrochemical cell with Pt/Nb electrodes (without a dividing membrane) where CO_2 reacts with 200 mL methanol in the presence of 11 g of CH_3OK and 30 g of bmimBr to produce 7.7 g/L DMC. The reaction yield is low (0.7% with respect to methanol) so that the excess methanol as well as CO_2 are recirculated until the reaction is completed. The synthesis is carried out at 30 °C, and the atmospheric pressure during 48 h under the constant-potential conditions. The best results in terms of the yield have been obtained at 5.5 V, achieving a final DMC concentration of 85 mmol/L (0.9% w/w); these results[19] are considered for the LCA data. The experimental work has not included separation and purification of DMC so that they have been simulated in Aspen HYSYS[40] as discussed below.

Simulation of the Separation and Purification Process. The reported kinetic model[19] has been used in MATLAB[41] to estimate the composition and flows of the components.[18,19] Using the MATLAB-HYSYS interface, the results from the model have been imported into HYSYS to simulate the separation and purification process. The UNIQUAC binary model from Aspen Properties has been used to calculate the physical properties of the mixtures DMC−methanol and DMC−water.[34,42] Finally, Aspen Energy Analyzer has been used to explore various heat integration opportunities.

The corresponding process flowsheets for the two process alternatives can be found in the Supporting Information in Figures S1 and S2, together with the summary of mass and energy balances in Tables S1 and S2. The first alternative, hereafter referred to as "El-chem. (1)" considers the use of water as the entrainer in the extractive distillation to separate the DMC-methanol azeotrope; the second process, referred to as "El-chem. (2)", uses aniline instead. The model for El-chem. (1) is based on the information reported in Ginnasi and Passoni[33] and for El-chem. (2), the data have been sourced from Hsu et al.[34] As mentioned earlier, CH_3OK and bmimBr are separated from the DMC−methanol mixture in a flash unit since both have a negligible vapor pressure.[43,44]

Inventory Data. The inventory data are given in Tables 2 and 3. The former summarizes the data used to model the LCA impacts of postcombustion capture and recovery of CO_2 from MEA, based on the inventory data in Singh et al.[32] A 90% efficiency is considered for the postcombustion CO_2 capture from a coal power plant.[51] The CO_2 capture also leads to other benefits, such as removal of SO_2, NO_x, and particulates from the flue gas. The system has been credited for the avoidance of these emissions, as indicated by the negative values in Table 2.[45] Table 3 shows the data for the production of DMC. The quantities of methanol, CO_2, and the entrainers have been estimated by MATLAB-HYSYS simulation. Methanol and CO_2 consumption are based on stoichiometric values, used up once the reaction is completed. The actual amounts of methanol and CO_2 are higher as they are recirculated in the system until the reaction is completed (113.8 kg methanol/kg DMC and 0.57 kg CO_2/kg DMC). The amounts of CH_3OK and bmimBr have been obtained from the experimental data.[19] Both chemicals are assumed to be used for one year before being replaced, with negligible losses during that time. The life cycle inventory data for bmimBr were not available and instead the data for bmimCl have been used as a proxy.[37] This can be justified because 1-methylimidazole is used in the production of both bmimBr and bmimCl. The electrodes for the reactor are considered as consumables with a lifespan of 1 year. The lifetime of the plant is assumed to be 20 years. The formation of byproducts in the electrochemical process (dimethyl ether and dimethoxymethane) has not been considered as a 100% selectivity has been assumed owing to a lack of data.

The electricity requirements for the electrochemical cell have been obtained from the experimental data[19] and own estimations (see the Supporting Information). Pumping

DOI: 10.1021/acssuschemeng.5b01515
ACS Sustainable Chem. Eng. 2016, 4, 2088−2097

requirements have been calculated as a function of the pressure drop in the electrochemical cell, assuming a conservative pressure drop of 2 bar and the motor and electric efficiencies of 50% and 90%, respectively. The electricity for pumping is assumed to be sourced from the Spanish grid. The electricity for the electrochemical reactor is assumed to be generated by solar photovoltaics as electrochemical processes are energy intensive and need to use renewable energy to be sustainable, as discussed in a previous study.[46] The amount of utilities required (steam and cooling water) have been estimated in HYSYS and Aspen Energy Analyzer. Steam is assumed to be produced from natural gas with a 90% efficiency (steam low pressure 10 bar, LHV 2.78 MJ/kg; medium pressure 40 bar, 2.80 MJ/kg; high pressure 90 bar, 2.74 MJ/kg). The environmental impacts of cooling water have not been taken into account because of their negligible impact in comparison to steam or electricity.

The quantity and composition of the waste streams have been estimated from the HYSYS output streams. The life cycle impacts of their management have been sourced from Ecoinvent,[39] assuming the liquid stream is sent to a wastewater treatment plant with mechanical, biological, and chemical processes, including sludge digestion. The organics purge is incinerated (flared) with no energy recovery. The solid waste from CO_2 capture is landfilled.

All relevant transport has been considered, assuming that all chemicals (except CO_2) are transported to the plant by road for 100 km in 32 t trucks.

The system has been credited for the GWP avoided by capturing CO_2 to produce DMC assuming the stoichiometric ratio of 0.49 kg CO_2 eq. captured per kg of DMC (see the reaction for route VI in Table 1). According to recent CCU literature,[47−50] the amount of CO_2 used in the process does not equal the amount of avoided CO_2 emissions to the atmosphere, with the exception of ideal sources (e.g., direct utilization of atmospheric CO_2), where systems are credited with −1 kg CO_2 eq. per kg of CO_2 used. Hence, the calculation of CO_2 credits in this work considers the environmental impacts of the capture process for CO_2. According to the inventory in Table 2, the capture process is estimated to generate 0.19 kg CO_2 eq., mainly due to electricity requirements, and avoids the emission of 1 kg of CO_2 per kg CO_2 captured. Hence, the total life cycle GWP is equal to GWP = 0.19−1 = −0.81 kg CO_2 eq./kg CO_2 captured. Another study estimated −0.86 kg CO_2 eq./kg CO_2 captured,[51] based on the conversion of the emissions from a 1 MWh power plant, which agrees well with the result obtained in the current study.

Oxidative Cabonylation Process. The inventory data for the Eni process are detailed in Table 2. They have been sourced from the available commercial data[36] and the Ecoinvent database.[39] CO is assumed to be produced by coal gasification using CO_2, which is also coproduced in the reactor and treated as a waste stream, as shown in Table 3.[36] It has been modeled based on the CO production process available in Ecoinvent. The amount of coal required has been obtained from the stoichiometric calculations assuming the coal composition of $C_{240}H_{90}O_4NS$. Oxygen is assumed to be obtained by cryogenic air separation. CuCl has not been considered owing to a lack of data. The stream purged from the organics removal section contains methyl chloride which is incinerated.[36]

RESULTS AND DISCUSSION

As mentioned in the Goal and Scope of the Study section, the emphasis is on the GWP, and hence these results are discussed first, followed by the other environmental impacts.

Global Warming Potential. As can be observed in Figure 3, GWP of the electrochemical process is estimated at 94.5 kg

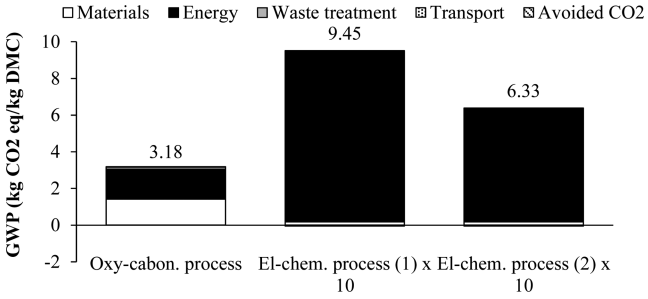


Figure 3. Global warming potential (GWP) for the systems under study. Oxy-carbon.: oxidative carbonylation (Eni) process. El-chem. (1): electrochemical process with water as the entrainer. El-chem. (2): electrochemical process with aniline as the entrainer. Some values have been scaled to fit on the scale. The original values can be obtained by multiplying the value shown on the *y*-axis by the scaling factor shown on the *x*-axis.

CO_2 eq./kg DMC for El-chem. (1) and 63.3 kg CO_2 eq./kg DMC for El-chem. (2). These values include the credit for the avoided CO_2 emissions (0.49 kg CO_2 eq./kg DMC) but are still on average 25 times higher than the GWP of the Eni process, which is equal to 3.2 kg CO_2 eq./kg DMC. The reason for such a large difference in the GWP is that the electrochemical process has a very low yield (0.7%) and produces a very diluted product (0.9% w/w). Therefore, the energy requirements for DMC separation are high: 1324 MJ/kg DMC for El-chem. (1) and 968 MJ/kg DMC for El-chem. (2), compared to the Eni process which needs 22.7 MJ/kg DMC (see Table 3). As a result, energy consumption contributes 98% to the total GWP (Figure 3), 83% of which is due to CO_2 emissions associated with burning of natural gas to generate steam. El-chem. (1) requires more energy than El-chem. (2) because water enhances the relative volatility between methanol and DMC less than aniline.

The contribution of the raw materials to the total GWP is small (2%) and that of waste management and transportation negligible. At 0.1 kg CO_2 eq./kg DMC, the contribution of CO_2 capture and recovery is also negligible. Among the raw materials, bmimBr is the main contributor to the GWP (64%), followed by methanol (32%); CH_3OK and CO_2 capture and recovery contribute around 3% each (see Figure 4). For bmimBr, the majority of the impact is due to 1-methylimidazole used in its production (76%), to which ethylene glycol contributes most (48%). The contribution of the raw materials becomes more significant as the process yield increases, as discussed later in the Improvement opportunities section. The avoided CO_2 in the electrochemical processes is estimated at −0.49 kg CO_2 eq./kg DMC and the total GWP of El-chem. (1) and El-chem. (2) without the CO_2 credits is 94.96 and 63.76 kg CO_2 eq./kg DMC, respectively. Hence, the contribution of the credits to the GWP reduction is small (<1%) compared to the total GWP owing to the significant contribution of energy consumption (and thus barely visible in Figure 3).

DOI: 10.1021/acssuschemeng.5b01515
ACS Sustainable Chem. Eng. 2016, 4, 2088−2097

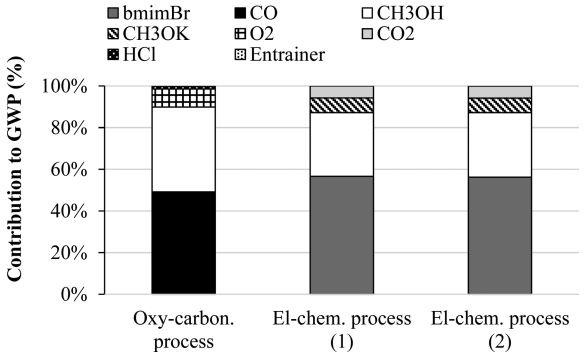


Figure 4. Contribution of raw materials to the global warming potential (GWP) for the systems under study. Oxy-carbon. process: oxidative carbonylation (Eni) process. El-chem. (1): electrochemical process with water as the entrainer. El-chem. (2): electrochemical process with aniline as the entrainer.

For the Eni process, energy consumption is also the main hot spot, contributing 51% to the total GWP (Figure 3). However, the raw materials follow closely with 44%, with the rest of the impact being from waste management (4%) and transportation (1%). Around 90% of the contribution from energy is due to steam used for the separation. As shown in Figure 4, the majority of the impact from the raw materials is due to CO (49%) and methanol (40%). This is again due to the energy required for their production.

Therefore, as these results suggest, the amount of CO_2 sequestered by producing DMC is several orders of magnitude (~129−193 times) lower than the CO_2 eq emissions generated during its sequestration and, at current process yield, it has a negative carbon balance while also generating other impacts, as discussed in the following section.

Other Environmental Impacts. Similar to GWP, all other impacts are much higher for the electrochemical than the Eni process, ranging from 11 times higher EP to 111 times higher $ADP_{elements}$ (Figure 5 and Table S3 in the Supporting Information). This is largely due to the use of energy and bmimBr. The results show that 1-methylimidazole is the main contributor to most environmental impacts related to bmimBr, ranging from 64% to 81% for POCP and HTP, respectively. The exception is ODP, where 1-chlorobutane accounts for 55% of the total impact, as opposed to 44% from 1-methylimidazole. This is mainly due to the use of HCl in the manufacture of 1-chlorobutane. With respect to energy, electricity is the main contributor for most environmental impacts except for ADP, ODP and POCP, where the steam contributes the most. The impacts from waste treatment and transport are negligible. However, as mentioned earlier, the coproducts from the process (dimethyl ether and dimethoxymethane) which could be used as alternative fuels for fuel cells,[52,53] have not been considered. If included, the system would be credited for their production and the impacts would be lower than estimated here. On the other hand, the coproducts would also reduce the DMC yield and additional energy would be required for the separation process, which would increase the impacts. Estimations of these opposing effects are not possible at present owing to a lack of data.

For the Eni process, the main contributors to the impacts are the raw materials, particularly CO and methanol. The exception

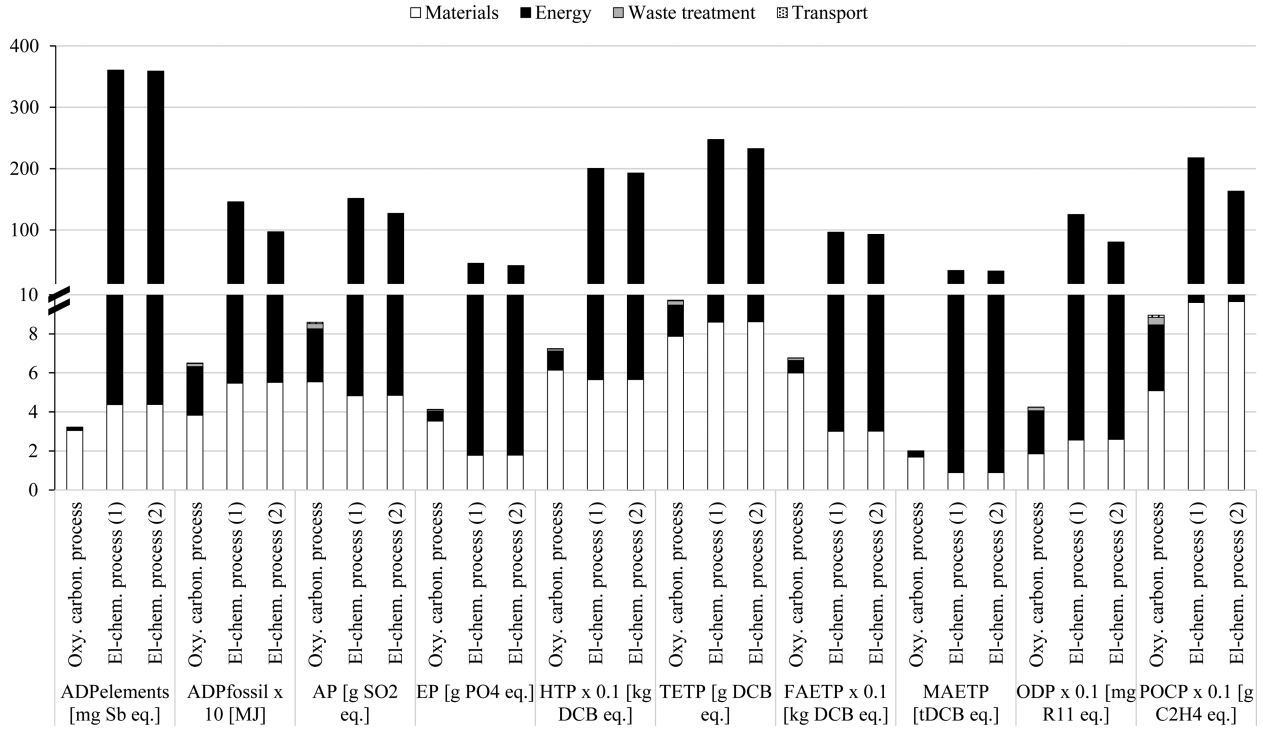


Figure 5. Environmental impacts other than the global warming potential for the systems under study. All impacts expressed per kg DMC (98% w/w). The values for some impacts have been scaled to fit on the scale. The original values can be obtained by multiplying the value shown on the *y*-axis by the scaling factor given on the *x*-axis. $ADP_{elements}$: abiotic depletion potential of elements. ADP_{fossil}: abiotic depletion potential of fossil resources. AP: acidification potential; EP: eutrophication potential. HTP: human toxicity potential. TETP: terrestrial ecotoxicity potential. FAETP: freshwater aquatic ecotoxicity potential. MAETP: marine aquatic ecotoxicity potential. ODP: ozone layer depletion potential. POCP: photochemical oxidant creation potential. The numerical values for all the impacts can be found in Table S3 in the Supporting Information.

DOI: 10.1021/acssuschemeng.5b01515
ACS Sustainable Chem. Eng. 2016, 4, 2088−2097

Table 4. Comparison of the GWP with the Literature for Different DMC Routes

source	route	GWP (kg CO_2 eq./kg DMC)	system boundaries	primary data	secondary data	impact assessment method
Monteiro et al.[20]	IV	0.86	cradle to gate	process simulation (HYSYS)	WAR database	Brazilian Environmental Agency, Environmental Protection Authority of Australia
	V	0.34				
Kongpanna et al.[22]	II	0.52	gate to gate	process simulation (Aspen Plus)	not reported	US EPA and IPCC emission factors
	IV	0.45				
	V	2.94				
Aresta and Galatola[23]	I	116	cradle to gate (excluding MeOH)	mass and energy balances	not reported	CML 2001
	V	29.4				
Current study	II	3.18	cradle to grave	process simulation (MATLAB and HYSIS)	Ecoinvent	CML 2001
	El-chem. (1)	9.45				
	El-chem. (2)	6.33				

Table 5. Comparison of Other Environmental Impacts with the Literature for Different DMC Routes

				electro-chemical process (this study)	
	route I (Aresta and Galatola[23])	route V (Aresta and Galatola[23])	route II (this study)	El-chem. (1)	El-chem. (2)
AP (g SO_4/kg DMC)	737	199.5	8.1	151	127
EP (g PO_4/kg DMC)	33.8	10.5	4.1	46	42
ODP (mg R11/kg DMC)	80.7	6.6	0.4	12.5	8
POCP (g C_2H_4/kg DMC)	26.5	6.7	0.9	21.8	16.3

is ODP because of the use of natural gas for steam and the associated halon emissions in its life cycle.

Comparison of Results with the Literature. As mentioned earlier, the Eni process (route II) is currently the dominant commercial route for producing DMC. The other routes are no longer in use (e.g., phosgenation of methanol (route I) due to high toxicity of phosgene, and carbonylation of methanol via methyl nitrite (route II) due to the need of an ammonia oxidation unit for large capacities and unstable intermediates from the safety point of view) or are still under development (ethylene carbonate transesterification (route IV) and urea transesterification (route V)). Nevertheless, for completeness, the results from the current study are compared to the LCA results for the other routes found in the literature. To our knowledge, only three other studies exist, for routes I, II, IV, and V (see Table 4); there are no studies for routes III and VI.

Two of these estimated only GWP,[20,22] with Aresta and Galatola[23] also reporting the results for four other impacts (AP, EP, ODP and POCP). However, the studies used different system boundaries, databases and life cycle impact assessment methods (see Table 4) so that their results are not directly comparable. Nevertheless, they provide an indication of the impact ranges for different routes.

As can be observed from Table 4, the phosgene route (I) has the highest GWP reported in the literature (116 kg CO_2 eq./kg DMC).[23] This is 47% higher than the impact from the electrochemical alternative considered here (63.3−94.5 kg CO_2 eq./kg DMC) and 37 times greater than the value for route II (the Eni process) estimated in this work (3.2 kg CO_2 eq./kg DMC). The latter is six times higher than the GWP reported by Kongpanna et al.[22] (0.52 kg CO_2 eq./kg DMC). However, Kongpanna et al. considered only a gate to gate system, excluding the upstream activities such as carbon monoxide and methanol production, which could explain this difference in the results.

Furthermore, Aresta and Galatola[23] found that GWP of the urea route (V) was 29.4 kg CO_2 eq./kg DMC, which is 86 times higher than the result reported by Monteiro et al.[20] (0.34 kg CO_2 eq./kg DMC) and 10 times higher than those reported by Kongpanna et al.[22] (2.94 kg CO_2 eq./kg DMC). Such disparity in the results is because Aresta and Galatola assumed that the energy for CO_2 recovery is electricity sourced from the grid (representing a "worst case"), as opposed to the studies of Monteiro et al. and Kongpanna et al., where CO_2 production was not considered.

As mentioned above, Aresta and Galatola[23] also estimated four other impacts in addition to the GWP; these results are compared in Table 5 to the impacts from the electrochemical and Eni processes calculated in the current study. As can be seen, route I appears to be the worst option for AP, ODP, and POCP while the electrochemical route is the least preferred for EP. The Eni process is the best option across all the impacts considered in the literature.

Improvement Opportunities. Based on the findings discussed in the previous sections, it is clear that the environmental impacts from the electrochemical process must be reduced significantly to make it environmentally (and economically) viable. Since energy consumption is the main hot spot in the system, a possible way to achieve this would be to improve the current yield of the electrochemical reaction to increase the concentration of DMC in the mixture, which would in turn reduce the amount of energy needed for the separation process. As the process is still under development, this could be achieved through further research into different materials for the electrodes, different ionic liquids and by optimization of operating conditions in a scaled-up process. Consideration of these aspects is beyond the scope of this paper but, instead, to guide future developments, a range of potential yields from 5%−50% (with respect to methanol) is explored to identify the minimum yield that would be required to reduce the impacts to at least the level comparable to the

DOI: 10.1021/acssuschemeng.5b01515
ACS Sustainable Chem. Eng. 2016, 4, 2088−2097

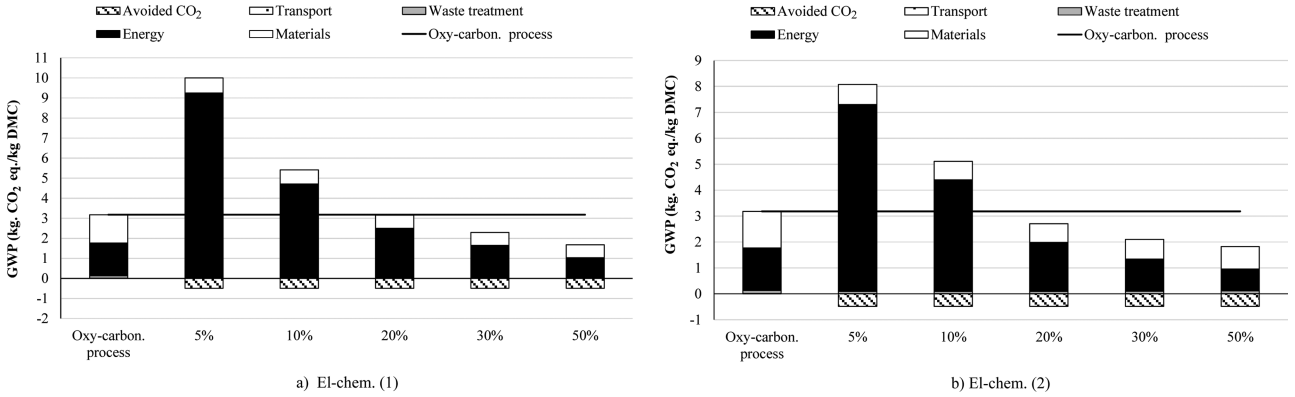


Figure 6. Influence on the global warming potential (GWP) of the electrochemical process yield (with respect to methanol) in comparison to the oxidative carbonylation process. The horizontal line represents the total GWP for the oxidative carbonylation process. For the GWP in the base case (0.7% yield) see Figure 3. DMC concentrations in the electrochemical cell for the corresponding yields 5%: 6.8% w/w; 10%: 13% w/w; 20%: 25% w/w; 30%: 35% w/w; 50%: 52% w/w. The numerical values for the GWP can be found in Table S4 in the Supporting Information.

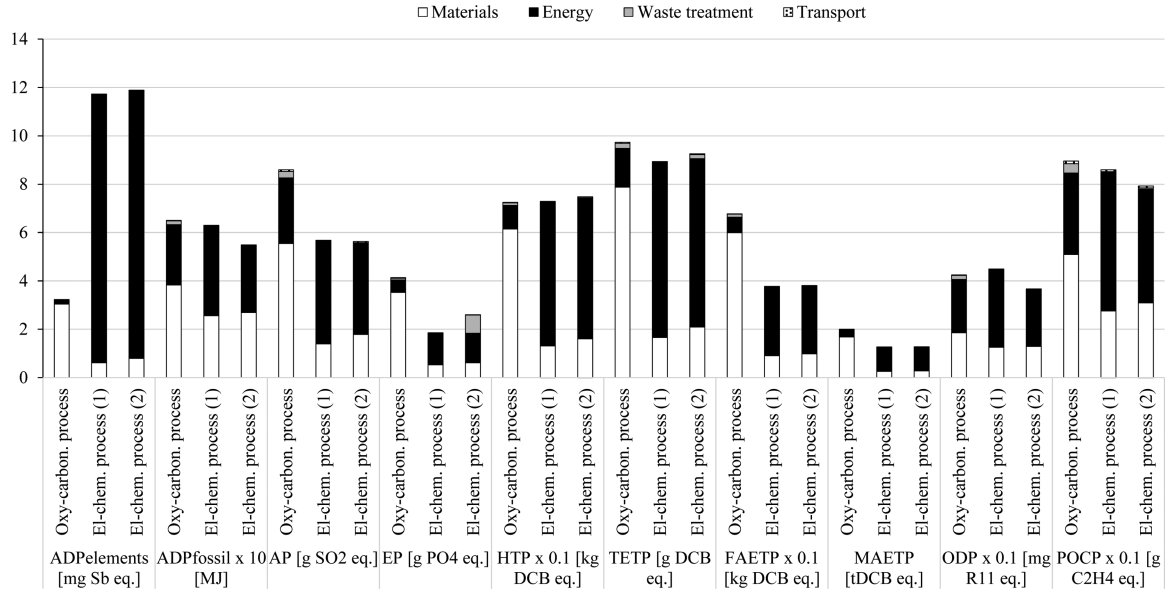


Figure 7. Environmental impacts (other than the global warming potential) for the electrochemical process yield of 20% (with respect to methanol) in comparison to the oxidative carbonylation process. For the impacts in the base case (0.7% yield) and the impacts nomenclature see Figure 5. The values for some impacts have been scaled to fit on the scale. The original values can be obtained by multiplying the value shown on the *y*-axis by the scaling factor given on the *x*-axis. The numerical values for all the impacts can be found in Table S5 in the Supporting Information.

commercial process. The results are discussed below, first for the GWP and then for the other impacts.

Global Warming Potential. As can be seen in Figure 6, GWP of the electrochemical process reduces progressively as the yield of the reaction increases and it becomes competitive with the commercial system at a yield of 20% and the corresponding DMC concentration in the cell of 25% w/w, achieving the total GWP of 2.4 kg CO_2 eq./kg DMC. This includes the credit for the avoided emission of CO_2 of 0.49 kg CO_2/kg DMC. The yield of 30% (35% w/w DMC) has a 46% lower GWP than the commercial process and the yield of 50% (52% w/w DMC), a 60% lower impact.

As mentioned previously, as the yield increases and the energy requirements drop, the contribution of the raw materials becomes more important, particularly for El-chem. (2) (Figure 6) because of aniline. Consequently, El-chem. (1) is a better option than El-chem. (2) for yields higher than 30%. Like the base case, the contributions of transport and waste treatment remain negligible.

Other Environmental Impacts. The effect of increasing the yield on the other impacts is shown in Figure 7. Since the yield of 20% is the minimum required to reduce GWP of the electrochemical process to the level comparable to the commercial system, the results are shown only for this yield as an illustration of the trend in impacts. It can be seen that, although energy consumption is still the main hot spot, the electrochemical process now has lower impacts than the Eni process for most categories, ranging from 7.8% lower POCP to 44% lower FAETP. The exceptions are $ADP_{elements}$, which is almost four times higher for the electrochemical process because of the production of solar photovoltaic modules, and to a lesser extent HTP, related to the life cycle of natural gas used to generate the steam. The latter is also the reason for El-chem. (1) having a slightly higher ODP than the commercial process (5.6%). There is little difference in the results between El-chem. (1) and (2) but, overall, the former represents a slightly better option.

DOI: 10.1021/acssuschemeng.5b01515
ACS Sustainable Chem. Eng. 2016, 4, 2088−2097

CONCLUSIONS

The environmental sustainability of the novel electrochemical route for producing dimethyl carbonate (DMC) from waste CO_2 has been assessed and compared to the commercial (Eni) system based on oxidative carbonylation. Two alternatives have been considered for the former, one using water and another aniline for extractive distillation. The results suggest that, at the present state of development, the electrochemical process is not sustainable because of low conversion to DMC and the related energy needed to separate the product from the reactants. For example, its global warming potential (GWP) is around 25 times higher than for the commercial process with the other life cycle impacts being 11−111 times greater. The process alternative using aniline for extractive distillation is slightly better than the one utilizing water. Energy consumption is the main hot spot for both alternatives, causing 98% of GWP and 96%−99% of the other impacts. The contribution of waste management and transport is negligible.

Therefore, future efforts in the development of the electrochemical process would need to focus on increasing the process yield to reduce energy consumption. The findings from this study indicate that a minimum yield at which the process is comparable to the commercial system is 20% and, beyond that, it becomes environmentally more sustainable for most impact categories considered here. This could be achieved through further research on alternative materials for the electrodes and ionic liquids as well as scaling up and optimization of operating conditions.

It is important that any future developments be evaluated iteratively through LCA to identify further improvement opportunities and eliminate the environmental hot spots systematically. As demonstrated in this work, as the process yield increases and energy consumption reduces, the raw materials become the main contributors to the impacts. Without applying life cycle thinking and LCA, these improvement opportunities may be missed and suboptimal process configurations developed, not only environmentally but also economically—the lower material and energy requirements and related impacts, the lower the costs. This is particularly important at the early stages of technology development where there are more degrees of freedom and different alternatives can be incorporated more readily. As illustrated by the example of the electrochemical process, combining LCA with the experimental data and process simulation at the outset can play a key role in delivering processes that are more sustainable by design.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b01515.

Energy requirement calculations, simulation flowsheets, and material and energy balances for the electrochemical process (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: garciahmi@unican.es. Tel.: +34 942 20931. Fax: +34 942 201591.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was funded by the Spanish Ministry of Economy and Competitiveness (MINECO) project CTQ2013-48280-C3-1-R and by the UK Engineering and Physical Sciences Research Council under the 4CU Programme Grant (EP/K001329/1). The authors are grateful for this funding. I.G.-H. would also like to acknowledge the FPI postgraduate research grant (BES-2011-047906) and thank A. Dominguez-Ramos and M. Margallo for their inestimable help.

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